

Carbon nanotube-modified LiFePO₄ for high rate lithium ion batteries

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Abstract: A hybrid cathode material for high rate lithium ion batteries was prepared by ball-milling and spray-drying a slurry containing LiFePO₄ nanoparticles, glucose and carbon nanotubes (CNTs) in water, followed by pyrolysis at 600 °C for 6h under a gas mixture of 5% H₂ in Ar. CNTs with a large aspect ratio form a continuous conductive network connecting the LiFePO₄ nanoparticles and amorphous carbon, which significantly reduces the electrical resistance of the cathode. The hybrid material can deliver a specific capacity of 99 mAh/g at a 50 C charge/discharge rate. An excellent cycling performance was also demonstrated, with a capacity loss of less than 10% after 450 cycles at a 10 C rate.

Key Words: LiFePO₄; Carbon nanotubes; Conductive framework; High rate cathode materials

1 Introduction

Rechargeable lithium ion batteries (LIBs) with a high energy and a high power density have rapidly conquered the consumer market of advanced portable electronics in recent years and are now considered as a candidate of next generation power source for future electric vehicles (EVs), hybrid EVs (HEVs), and plug-in hybrid EVs (PEVs). To meet the dramatically-increased demand for the emerging applications of EV, HEV and PEV, the electrode materials for LIBs with a high safety, a high power density and a long cycle life are urgently required. Among the known cathode materials, olivine lithium iron phosphate (LiFePO₄) is considered as an appealing candidate. LiFePO₄ possesses advantages of potentially low cost, rich resources, and environmental friendliness. It also has a high lithium intercalation voltage of 3.4 V and a high theoretical capacity of 170 mAh·g⁻¹. Although it displays a plenty of attractive characters, the low electronic/ionic conductivity of LiFePO₄ remains a major drawback, hindering its high rate applications. In order to further promote the power performance of LiFePO₄, considerable efforts have been made by decreasing the particle size^[1–6] and coating LiFePO₄ particles with conductive carbons^[7–12]. Doping of divalent (Mg²⁺, Mn²⁺, Ni²⁺, Cu²⁺) or supervalent ions (Al³⁺, Cr³⁺, Zr⁴⁺, Nb⁵⁺) either in Li site (M1) or in Fe site (M2) has also been demonstrated to be able to improve its electronic conductivity successfully^[13,14].

As the nanosized particles can reduce the lithium-ion diffusion path, the nanostructural design or particle size

reduction is an effective way to improve the rate capability of LiFePO₄^[16]. LiFePO₄ with special morphologies such as nanofibers or nanowires also demonstrated potential for high power applications^[17,18]. Until now, two typical approaches have been developed to synthesize LiFePO₄ nanoparticles. One strategy includes various soft chemical methods, such as sol–gel^[19–22], hydrothermal^[20–22] and solvothermal methods^[23], as they provide intimate mixing of the component elements in solution, allowing the formation of finer particles by rapid homogeneous nucleation of LiFePO₄. The main disadvantage is that such tedious process increases the manufacturing cost and leads to a unwanted particle growth. Another method is high-energy ball milling. According to the report of Taniguchi^[24] and Fey^[25], the ball-milling method decreased particle size, thereby reducing the length of diffusion and improving the reversibility of the lithium ion intercalation/deintercalation. Another factor limiting the performance of LiFePO₄ is its low electronic conductivity. The carbon-coated LiFePO₄ particles can improve room-temperature electrochemical performance greatly^[26], therefore various organic or polymeric precursors have been used as carbon sources for the coating. However, these processes cannot totally solve the electronic conductivity problem of LiFePO₄. As the pyrolyzed carbon are generally nano-size particles, the LiFePO₄/carbon particles are still in point-to-point contact in the electrode, which is not an ideal three dimensional continuous carbon conductive network. Organic pyrolytic carbon usually exhibits a lower electronic conductivity which hinders a further electrochemical

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performance enhancement of LiFePO_4 materials.

In recent years, the applications of carbon nanotubes (CNTs) in LIBs have attracted intense research interest because of their extraordinary thermal and mechanical stability and high electronic conductivity. According to Liu *et al.* [16], dispersing CNTs on the surface of microsize active materials homogeneously has the following advantages: i) forming a continuous conductive network on the bulk of electrodes to decrease electrode polarization, beneficial to the improvement of cyclic performance; ii) improving the adsorption and immersion of electrolyte on the surface of electroactive materials to facilitate the electrode reaction kinetics; and iii) as a buffer among electroactive materials due to their superior resiliency, restraining cracking and crumbling, and keeping the integrity of the electrode. Endo *et al.* [27] firstly reported that the cycling performance of the anode could be improved significantly by adding graphitized carbon nanofibers into graphite anode as conductive filler. CNTs have been used in LiCoO_2 , LiFePO_4 [28–30], and $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ [31,32], cathodes leading to a $\sim 10\%$ improvement in the reversible capacity compared with carbon black. Besides as conductive additives, CNT-containing composite materials, such as SnO_2/CNT [33], SnSb/CNT [34], CuO/CNT [35], $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ [36], TiO_2/CNT [37] and $\text{V}_2\text{O}_5/\text{CNT}$ [38] were also investigated. However, in these cases, complicated wet-chemistry methods were usually employed during the preparation, which hinders the large scale, practical applications of these materials in LIBs.

In this study, we develop a method for preparing microsphere-containing nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ by a combined ultrafine ball milling and spray-drying method. In the hybrid material, CNTs form continuous frameworks that connect the nano- LiFePO_4/C particles. Compared with the conventional carbon coated micro or nano sized LiFePO_4 , the nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ hybrid exhibits a significantly-improved rate capability and cycling performance. Since the preparation procedure is very simple, the CNT enhanced hybrid cathode can be a promising candidate for real applications in high rate LIBs.

2 Experimental

Commercial LiFePO_4 with a 1.5% carbon content and about 2–4 μm average particle diameter were purchased from Aleees Company (Taiwan, China) and used as the raw material. For the fabrication of the nano- LiFePO_4/C particles, 85% (weight percent) of the commercial LiFePO_4 powder and 15% glucose were ultrafinely milled using 0.5 mm zirconia balls and ethanol as a dispersant. After the ball milling for 1.5 h, the resultant slurry was sprayed and dried to get the nano- LiFePO_4/C precursor. Then the precursor was annealed at 600 °C under Ar/H_2 (5% vol. H_2) gas flow for 6 h to obtain the spherical materials. Under these conditions, 1 g of glucose yield about 0.24 g carbon, and the content of carbon in the material was about 5.0%–6.0%.

For the nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ hybrid preparation, the raw LiFePO_4 and 3% glucose were firstly ultrafine ball milled for 1.5 h, and then 3% graphitized CNTs (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences) were added into the slurry. Then the mixed slurry was milled for another 2 h at 300 r/min to uniformly disperse the CNTs. Finally, the slurry was spray dried and sintered at 600 °C in Ar/H_2 (5% vol. H_2) for 6 h to yield the resultant nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ hybrid, the overall carbon content of this hybrid material is also about 5.0%–6.0%.

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, FEI Nova Nano 430), transmission electron microscopy (JEOL, 2010) and XRD (D-MAX/2400, Cu K α). The residual carbon content of the resultant LiFePO_4 hybrid materials was determined by carbon sulfur analyzer (LECO, CS 400).

Electrochemical experiments were performed using CR2032-type coin cells. For preparing working electrodes, a dispersant of the as-synthesized hybrid materials, carbon black, and poly(vinyl difluoride) (PVDF) at a weight ratio of 60:25:15 in 1-methyl-2-pyrrolidinone (NMP) was pasted on pure Al foil. Typical loadings for the 50 μm -thick coatings were 5 $\text{mg}\cdot\text{cm}^{-2}$ of cathode powder. Microporous polypropylene separator (Celgard 2400) was used as a separator. The electrolyte consisted of a solution of 1 mol/L LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, in volume) obtained from Novolyte Chemical Co. Ltd. Pure lithium foil was used as a counter electrode. The cells were assembled in an argon-filled glove-box. Galvanostatic charge-discharge cycles were tested by LAND CT2001A multi channel battery testers at various current densities from 1 to 50 C (1 C=165 mAh/g) between 4.2 and 2.5 V vs Li^+/Li at room temperature. Note that under the test-voltage-range conditions, CNTs or pyrolysis carbon is stable and does not react with lithium, nonetheless we include the mass of residual carbon when calculating the specific capacity of CNTs hybrid LiFePO_4 materials. Conductivity measurements were made on disc-shaped fired samples by a four-point d.c. method. Four-point conductivity measurements were made on discs of ~ 8 mm diameter and ~ 0.6 mm thickness, and a SZT-2 instrument (Suzhou, China) was used. AC impedance spectrum was measured by a Solatron 1260/1287 Impedance Analyzer in the frequency range from 10 mHz to 100 kHz with a potential perturbation at 10 mV.

3 Results and discussion

Fig. 1 shows the XRD patterns of the raw LiFePO_4 , ball milled LiFePO_4 , nano- LiFePO_4/C and nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ samples. All the spectra fit a standard LiFePO_4 olivine structure indexed by orthorhombicPnmb, and no impurity peaks can be found. Compared with raw LiFePO_4 , the XRD pattern of the ball milled LiFePO_4 displays a broader shape, indicating the reduced crystallite size and poor crystallinity caused by the ball-milling process. After combined with CNTs and glucose pyrolytic carbon, the surface defects disappeared,

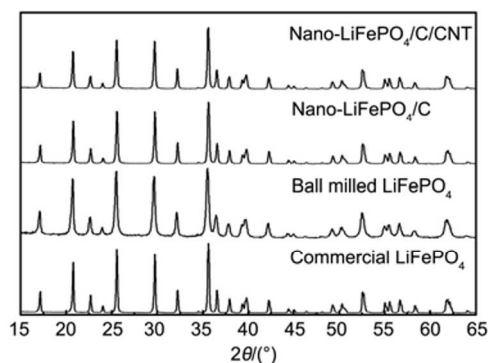


Fig. 1 XRD patterns of the raw, ball milled, nano- LiFePO_4/C and nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ samples.

and the particle sizes of both samples increased slightly, as shown in the XRD spectra of the nano- LiFePO_4/C and nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$.

Fig. 2a shows that the typical size of the raw LiFePO_4 is in the range of 2–4 μm . CNTs with a diameter and length of about 30–50 nm and 2–5 μm , respectively, are shown in Fig. 2b. Fig. 2c shows that the obtained hybrid nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ is in regularly-spherical shape. Fig. 2d and 2e show that the CNTs intertwine with nano- LiFePO_4/C particles to form a three-dimensional framework. These CNTs well-integrated with LiFePO_4/C may provide efficient electron transportation channels that facilitate the high rate

charge/discharge. From the high resolution TEM image as shown in Fig. 2f, the CNTs firmly attach with the LiFePO_4 particles, indicating that the CNT frameworks are rather stable.

Fig. 3a, b and c show the charge/discharge curves. From Fig. 3a, it can be seen that the commercial carbon coated LiFePO_4 shows high specific capacities of $\sim 158 \text{ mAh/g}$ at 0.2 C and 122.3 mAh/g at 1 C. At higher charge/discharge rates, it exhibits much lower specific capacities of 89.5 mAh/g and 54.1 mAh/g at 5 C and 10 C, respectively. From Fig. 3b and c, we can clearly see that the nano- LiFePO_4/C and nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ show a much improved charge/discharge performance at high rates. Nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ hybrid exhibit the best performance, it delivers specific capacities of 127.1, 119.2 and 99 mAh/g at 10, 20 and 50 C rates, respectively, whereas 110.3, 87.5 and 59.2 mAh/g were obtained for the nano- LiFePO_4/C at the same rates.

Potential difference can represent the degree of polarization of the electrode. As shown in Fig. 3 a-c, by adding CNTs in hybrid materials, the potential difference of LiFePO_4 can be significantly decreased from 212.2 to 72.5 mV at 1 C rates. Fig 3d also compares the polarization between the charge and discharge plateau for the three electrodes at high rates. It can be seen that the polarization for the nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ electrode are much smaller than those

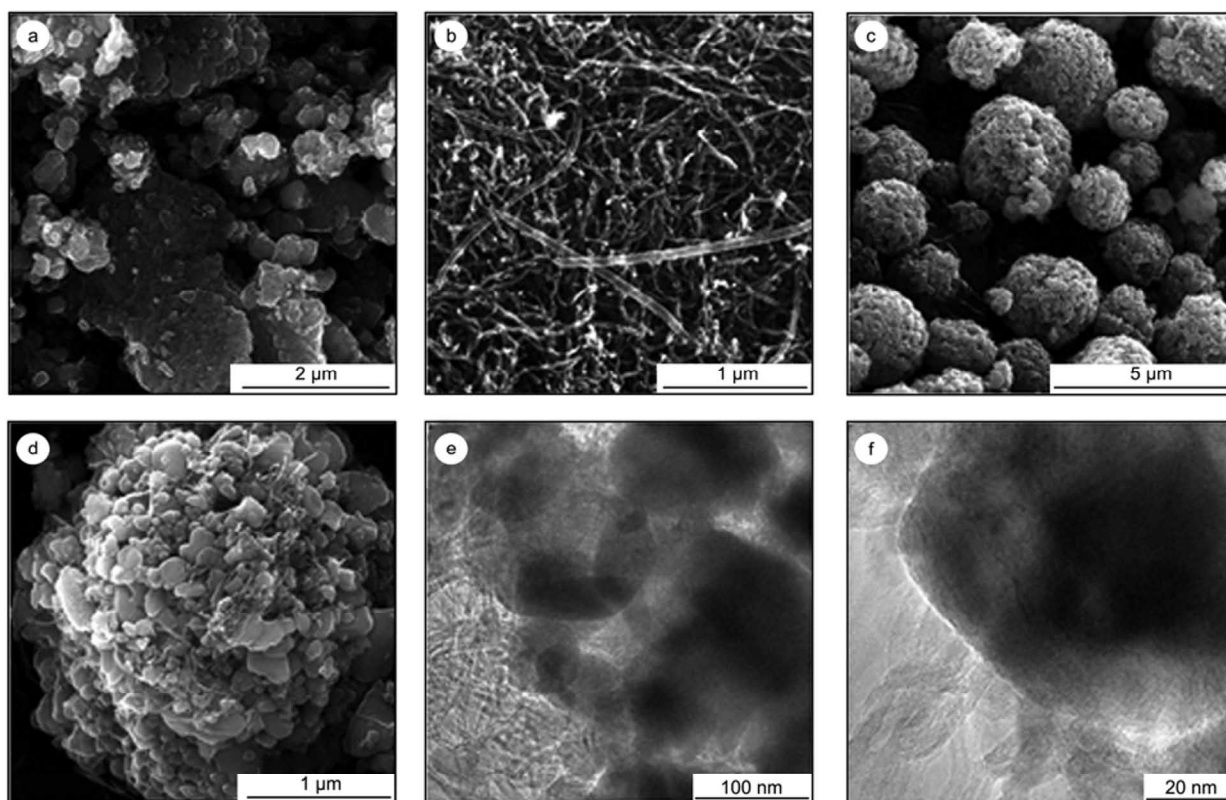


Fig. 2 SEM images of (a) the raw sample, (b) CNTs, (c,d) nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$, (e,f) TEM images of the nano- $\text{LiFePO}_4/\text{C}/\text{CNT}$ hybrid at different magnifications.

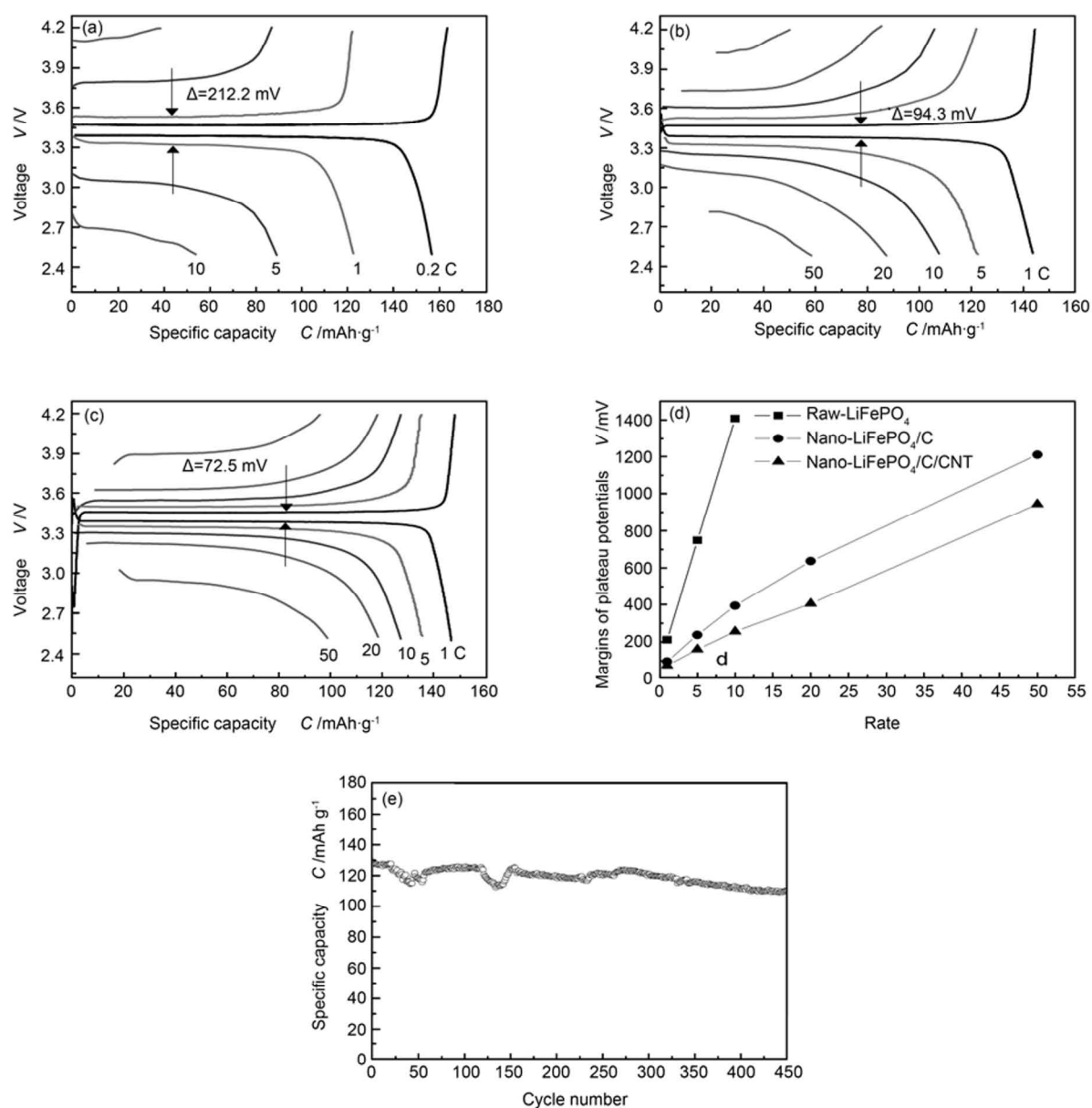
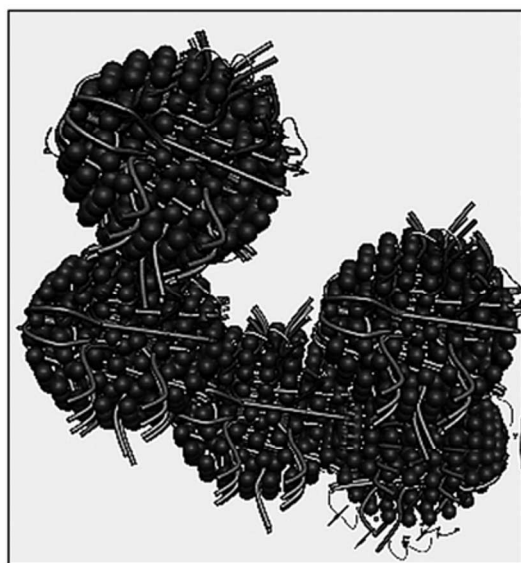


Fig. 3 Charge and discharge curves of the (a) raw LiFePO₄, (b) nano-LiFePO₄/C, (c) nano-LiFePO₄/C/CNT electrodes from 0.2 to 50 C, (d) comparison of the charge and discharge plateau potential difference, (e) cycling performance of n-LiFePO₄/C/CNT tested at 10 C rates between 2.5 and 4.2 V.

of the commercial LiFePO₄ and the nano-LiFePO₄/C electrode at discharge rates from 1 C to 50 C, which again indicates that the nano-LiFePO₄/C/CNT electrode has a better reaction kinetics, because of the improved electronic conductivity caused by the continuous CNTs frameworks. Fig. 3e shows the cyclic performance of the nano-LiFePO₄/C/CNT hybrid at 10 C charge/discharge rate. In the first cycle, the discharge capacity was 129.5 mAh/g, and it still remains at 110.5 mAh/g even after 450 charge/discharge cycles, a 85.3 % retention of the first discharge capacity.

Carbon content analysis shows that the final the

nano-LiFePO₄/C and the nano-LiFePO₄/C/CNT material contain about 5.1% and 5.9% carbon respectively. Scheme 1 illustrates the unique CNTs framework structure of the nano-LiFePO₄/C/CNT hybrid. Compared with commercial materials, the superior electrochemical performance of the hybrid material can be ascribed to the following factors: (1) nanosized particles can reduce the lithium-ion diffusion path and improve its rate capability; (2) higher carbon content can increase the total electronic conductivity, which is beneficial for the high rate performance and (3) more importantly, because of their one-dimensional structure and large aspect ratio, the integrated CNTs can form networks linking the nano LiFePO₄ particles. Together with their excellent electric



Scheme 1 Scheme of the structure of nano-LiFePO₄/C/CNT hybrid material.

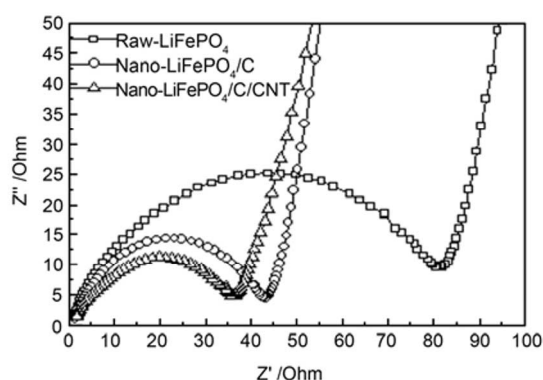


Fig. 4 EIS of the raw LiFePO₄, nano-LiFePO₄/C and nano-LiFePO₄/C/CNT.

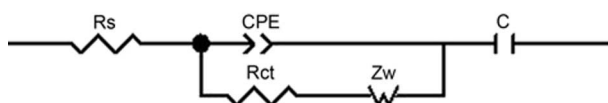


Fig. 5 Equivalent circuit used to model the impedance spectra shown in Fig. 4.

Table 1 Electronic conductivity of the raw LiFePO₄, nano-LiFePO₄/C and nano-LiFePO₄/C/CNT.

Samples	Commercial LiFePO ₄	Nano- LiFePO ₄ /C	Nano-LiFePO ₄ /C/CNT
C w/%	1.6	5.1	5.9
Electronic conductivity γ (S/cm) $\times 10^{-2}$	0.8	2.8	4.1

Table 2 Impedance parameters calculated from the equivalent circuits.

Materials	R_s	R_{ct}	$i^0/\text{mA}\cdot\text{cm}^{-2}$
Commercial	0.877	34.47	0.745
Nano- LiFePO ₄ /C	1.051	40.41	0.635
Nano- LiFePO ₄ /C/CNT	0.691	75.91	0.338

properties, the continuous CNTs framework offers a considerable benefit over traditional organic carbon coating in terms of the improvement of the electronic conductivity. As shown in Table 1, by adding CNTs, the bulk electronic conductivity of the LiFePO₄ hybrid material can be increased significantly, reaching a value of 0.041 S·cm⁻¹ at room temperature.

The electrochemical kinetics of the samples can be depicted from their electrochemical impedance spectra (EIS). Fig. 4 shows typical Nyquist plots of the samples, which are comprised of depressed semicircles in the high frequency region, a Warburg-type element in the low frequency region, and a steep sloping line deviated from 45° at the lowest frequencies. The Warburg region is attributed to solid-state diffusion of Li-ion into the bulk cathode material, while the steep sloping line reflects a capacitive behavior. This capacitive behavior is due to accumulation of the Li ions into the bulk [39]. All these features and relative parameters of the impedance spectra may be modeled by a modified Randles-Ershler equivalent circuit as shown in Fig. 5. R_s means lithium ions diffusion resistance arising from the electrolyte resistance and the cell components and R_{ct} represents charge-transfer resistance of the intercalation reaction. Calculated R_s , R_{ct} and exchange current density values are shown in Table 2. It can be seen that R_{ct} values of the nano-LiFePO₄/C/CNT reduced from 75.91 to 34.47 Ohms compared with raw materials. A lower charge transfer resistance is favorable for reducing polarization and increasing lithium ion moving depth, thereby it can improve the electrochemical performance. Based on the following equation [36], the exchange current densities can be calculated.

$$i^0 = RT/nFR_{ct}$$

Where R_{ct} means charge-transfer resistance and n is the charge transfer number during charge-discharge. Substituting experimental data into this equation, we can get exchange current densities. From Table 2, it can be observed that the exchange current densities of the nano-LiFePO₄/C/CNT and the nano-LiFePO₄/C are both higher than that of the raw materials and the nano-LiFePO₄/C/CNT cell has the biggest exchange current density.

4 Conclusions

A hybrid cathode material composed of LiFePO_4 nanoparticles, amorphous carbon, and carbon nanotubes frameworks was prepared by a combination of ball-milling and spray-drying and pyrolysis. The CNTs in the hybrid material form desirable frameworks interlinking the active LiFePO_4 nanoparticles, and thus improving the conductivity of the cathode significantly. As a result, the hybrid material with ~3% CNTs and ~2% pyrolyzed carbon delivered specific capacities of 127.1, 119.2 and 99.0 mAh/g at 10, 20 and 50 C rates, respectively. Even after 450 cycles, around 85.3 % of the capacities can be retained at all C rates. The desired high rate capability and cycling performance and simple synthetic process of the $\text{LiFePO}_4/\text{C}/\text{CNT}$ hybrid cathode make it a promising candidate for applications in high-rate LIBs.

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